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PATENT SPECIFICATION

1,058,304



NO DRAWINGS

1,058,304

Inventor: MANMOHAN SHARN

Date of filing Complete Specification (under Section 3 (3) of the Patents Act 1949) March 11, 1965.

Application Date: March 11, 1964.

No. 10566/64.

Application Date: July 28, 1964.

No. 30019/64.

Complete Specification Published: Feb. 8, 1967.

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ERRATA

SPECIFICATION No. 1,058,304

Page 1, Heading, *Inventor:* for "MANMOHAN SHARN" read "MAN MOHAN SHARMA"

Page 1, Heading, *Application Date:* for "March 11, 1964" read "March 12, 1964"

THE PATENT OFFICE
29th March 1967

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15 ~~diisopropylamine (DIPA)~~. Each of these amines has certain disadvantages. While
MEA is generally satisfactory for removing hydrogen sulphide and carbon dioxide, it is
not suitable for removing carbonyl sulphide, as it forms therewith compounds that can-
20 not easily be regenerated, so that some MEA is irretrievably lost. DEA does not suffer
from this disadvantage but it is more viscous and reacts only slowly with carbonyl
sulphide. It is also not so effective as MEA in removing hydrogen sulphide and carbon
dioxide. DIPA is in some respects rather better than DEA but it still reacts slowly with
carbonyl sulphide.

15

20

25 The present invention is based on extensive research carried out to discover whether
any other substances would be superior to MEA, DEA and DIPA in performance and
would be satisfactory for commercial operations, *inter alia* from the point of view of
costs of manufacture and use and of easy and substantially complete regenerability. This
research has resulted in the discovery of two classes of amines, viz. alkanolalkyl amines
and morpholines, which provide substantial improvements over the conventional amines.

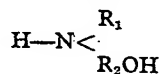
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30 According to the invention a process for the purification of a fluid which contains
hydrogen sulphide and/or carbon dioxide and/or carbonyl sulphide as impurities com-
prises treating the fluid with a liquid absorbent comprising an aqueous solution of at
least one amine of the group consisting of alkanolalkyl amines and morpholines, thereby
obtaining a fluid with a reduced impurity content and a liquid absorbent containing
absorbed impurities, and re-using at least part of the said liquid absorbent after des-
35 sorptive regeneration for treating a further quantity of the fluid to be purified.

30

The alkanolalkyl amines are secondary amines of the general formula:

35



in which R_1 stands for an alkyl group ($-C_nH_{2n+1}$) whereas R_2OH indicates an alkanol group ($-C_mH_{2m}OH$) (n may or may not be equal to m).

Suitable alkanolalkyl amines are, *inter alia*, ethanolmethyl amine (methylamino-

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Int. Cl.:—C 10 g 21/20

COMPLETE SPECIFICATION

Process for the Purification of Fluids

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a Company organised under the Laws of the Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the purification of fluids from impurities such as carbon dioxide, hydrogen sulphide and carbonyl sulphide.

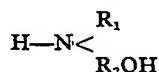
Liquid hydrocarbon oils, and also gases such as refinery gases and natural gas from various sources, often contain substantial amounts of sulphur-containing impurities and/or carbon dioxide, while the large-scale manufacture of ammonia for fertilizer production often entails removal of substantial amounts of carbon dioxide.

Various amines have been employed or suggested for removing such undesirable constituents, the most common being monoethanolamine (MEA), diethanolamine (DEA) and diisopropanolamine (DIPA). Each of these amines has certain disadvantages. While MEA is generally satisfactory for removing hydrogen sulphide and carbon dioxide, it is not suitable for removing carbonyl sulphide, as it forms therewith compounds that cannot easily be regenerated, so that some MEA is irretrievably lost. DEA does not suffer from this disadvantage but it is more viscous and reacts only slowly with carbonyl sulphide. It is also not so effective as MEA in removing hydrogen sulphide and carbon dioxide. DIPA is in some respects rather better than DEA but it still reacts slowly with carbonyl sulphide.

The present invention is based on extensive research carried out to discover whether any other substances would be superior to MEA, DEA and DIPA in performance and would be satisfactory for commercial operations, *inter alia* from the point of view of costs of manufacture and use and of easy and substantially complete regenerability. This research has resulted in the discovery of two classes of amines, viz. alkanolalkyl amines and morpholines, which provide substantial improvements over the conventional amines.

According to the invention a process for the purification of a fluid which contains hydrogen sulphide and/or carbon dioxide and/or carbonyl sulphide as impurities comprises treating the fluid with a liquid absorbent comprising an aqueous solution of at least one amine of the group consisting of alkanolalkyl amines and morpholines, thereby obtaining a fluid with a reduced impurity content and a liquid absorbent containing absorbed impurities, and re-using at least part of the said liquid absorbent after desorptive regeneration for treating a further quantity of the fluid to be purified.

The alkanolalkyl amines are secondary amines of the general formula:



in which R_1 stands for an alkyl group ($-\text{C}_n\text{H}_{2n+1}$) whereas R_2OH indicates an alkanol group ($-\text{C}_m\text{H}_{2m}\text{OH}$) (n may or may not be equal to m).

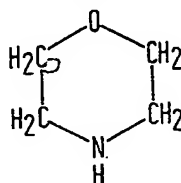
Suitable alkanolalkyl amines are, *inter alia*, ethanolmethyl amine (methylamino-

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ethanol, MAE), ethanolethyl amine (ethylaminoethanol, EAE), ethanol-n-propyl amine, ethanalisopropyl amine, n-propanolmethyl amines, isopropanolmethyl amines, n-propanolethyl amines, isopropanolethyl amines, n-propanol-n-propyl amines and isopropanolisopropyl amines.

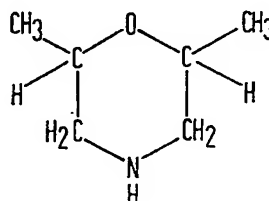
5 In the present specification the term "morpholines" stands for morpholine and its homologues.

Morpholine itself is a secondary amine of the formula:



10 and in its homologues one or more hydrogen atoms attached to one or more of the carbon atoms are replaced by alkyl groups.

Suitable morpholines are, *inter alia*, morpholine itself, 2,6-dimethylmorpholine (2,6-DMM):



15 2,6-diethylmorpholine, 2,3,5,6-tetramethylmorpholine, 2,3,5,6-tetraethylmorpholine, 2-methylmorpholine, 2-ethylmorpholine and 2-methyl-6-ethylmorpholine.

Those amines from the above two classes are usually preferred that have an intermediate boiling point, viz. between 120 and 200°C. For higher boiling compounds the viscosity will be so high and the carrying capacity (on a weight basis) so low that they tend to become unattractive, at least for the more common applications. For lower boiling compounds the degree of evaporation of the amines during regeneration and also during gas purification may well be sufficient to make the amine losses and/or the costs of preventing such losses (e.g. by the use of washing facilities for reclaiming amines from the treated fluid and/or the acid gases that leave the regenerator) objectionably high.

25 Amines according to the present invention that boil between 135 and 180°C are particularly preferred.

These particularly preferred amines include MAE (boiling point 155—159°C), EAE (boiling point 167—170°C) and 2,6-DMM (boiling point 147°C), which amines have the additional advantage of being easy and cheap to manufacture.

30 MAE can readily be made by reacting methylamine with ethylene oxide. Methyl amine is readily obtainable on a commercial scale and is relatively inexpensive. EAE is obtained in a similar way from ethylamine and ethylene oxide.

2,6-DMM is readily obtained from DIPA by dehydration.

35 The amines used may be pure compounds or of technical grade; in the latter case it may sometimes be desirable or necessary to apply one or more purification treatments to the compounds or their mixture before the liquid absorbent is put into use.

The amine content of the liquid absorbent may vary within wide limits, but is usually between 0.5 and 8 moles/l, and preferably between 1 and 6 moles/l.

40 It has been found that the presence of other components may sometimes be advantageous. Thus, components such as glycols (e.g. diethylglycol and triethyleneglycol) may also be present in the liquid absorbent, e.g. for water removal.

In a modification of the present process use is made of a liquid absorbent which contains one or more alkanolalkylamines and/or morpholines together with one or more

physical solvents for the impurities to be removed from the feed material. These modified liquid absorbents may either contain water or be free or substantially free from water.

5 Examples of suitable physical solvents that can be used in this modified process are cyclo tetramethylene sulphone and its derivatives, aliphatic acid amides, perhalocarbons (perhaloalkanes), N-alkylated pyrrolidones and N-alkylated piperidones. 5

10 The derivatives from the basic sulphone cyclo tetramethylene sulphone or thiophene tetrahydro-1, 1 dioxide (which is also known as sulfolane), should preferably have not more than 4, more preferably not more than 2, substituents selected from alkyl, aryl, arylalkyl, and/or alkoxy groups in the tetramethylene sulphone ring. Preference is usually given to substituent groups with 1—4 carbon atoms. 10

Sulfone itself is a particularly preferred species of this class of compounds.

15 Suitable amides are the dialkyl-N-substituted aliphatic acid amides, a preferred species being dimethyl formamide. Preferably the alkyl groups directly attached to the nitrogen atom have from 1 to 4 carbon atoms each, while an acid with 1 to 4 carbon atoms per molecule is preferred as well. 15

20 Apart from dimethyl formamide mentioned above, other species in this class include methylethylformamide, diethylformamide, propylmethylformamide, dibutylformamide, dimethylacetamide, methylethylacetamide, formamide and acetamide. 20

Suitable perhalocarbons include perfluoro alkanes such as perfluoro ethane and perfluoro butane as well as perchloroalkanes such as perchloropropane. 20

25 The N-alkyl pyrrolidones and N-alkyl piperidones used may have side-chains attached to the carbon atoms of the heterocyclic rings. If such side-chains are present they are preferably of the alkyl type and the total number of carbon atoms per side-chain is then preferably one or two. However, it is usually desirable to use unsubstituted N-alkylated pyrrolidones and piperidones. The alkyl substituent on the N atom may be any alkyl group, but preference is usually given to alkyl groups with 1 to 4 carbon atoms. N-methyl pyrrolidone is a particularly preferred physical solvent. 25

30 The amine content of the modified liquid absorbent is usually between 0.5 and 8 moles/l, and preferably between 1 and 6 moles/l, the balance of the liquid absorbent consisting of one or more physical solvents, and possibly but not necessarily other components. In this type of operation the presence of other components may sometimes be advantageous. Thus, liquid absorbents also containing a certain amount of water, e.g. in the range 1 to 30 wt.%, may sometimes be very suitable, particularly because of their lower viscosity and easier and cheaper regenerability. 30

35 These modified forms of the process according to the invention may be carried out in ways similar to those described in British patent applications No. 45,908/61 (Serial No. 972,140) and No. 8,759/64 (Serial No. 1,024,412). 35

40 The fluids to be purified in accordance with the present invention should of course be at least partly immiscible with the liquid absorbent used. 40

45 As impurities to be at least partly removed by the process according to the present invention, the feedstocks contain at least one of the following: hydrogen sulphide, carbon dioxide and carbonyl sulphide. Other impurities, such as carbon disulphide, hydrocyanic acid and mercaptans, may also be present in the feedstocks, and these impurities may also be removed to a certain extent in the operation of the present process, but for some of these other impurities this removal may be accompanied by the formation of non-regenerable compounds with the amine or amines used, thus giving rise to some deterioration of the liquid absorbent. 45

50 Examples of liquid feed streams are hydrocarbon oils from which hydrogen sulphide and frequently also carbonyl sulphide are to be removed. Particularly important examples of this category are the liquefied propane/propene fractions which contain both hydrogen sulphide and carbonyl sulphide and are obtained from the products of the cracking or thermal reforming of sulphur-bearing mineral oils. 50

55 Gaseous mixture which can advantageously be treated by the process according to the invention include natural gas, refinery gas, town gas, flue gas, and the hydrogen- and carbon monoxide-containing gases that are obtained by incomplete combustion of hydrocarbon materials or carbonaceous materials by means of air, oxygen-enriched air or oxygen, possibly in the presence of added steam. 55

60 The present process is particularly suitable for the purification of fluid streams (especially gases) that contain carbonyl sulphide. 60

The present liquid absorbents absorb carbon dioxide, carbonyl sulphide and hydrogen sulphide at a more rapid rate than the previously used amines under like conditions, which is a very important advantage.

This is substantiated by the results of a number of comparative experiments which were carried out to determine the absorption rates of various amines, using substantially pure carbon dioxide and carbonyl sulphide, at a temperature of 25°C and at atmospheric pressure. The amines were used in the form of one molar aqueous solution, and all experiments were carried out in the same jet reactor.

The results are given in the following Table, which sets out the relative rates of absorption (rate of absorption is defined as amounts absorbed per unit area of interface per unit of time), the rate for MEA, which was the arbitrary value unity in both cases, being used as the standard of comparison.

amine	test gas	
	carbon dioxide	carbonyl sulphide
MEA	1	1
DEA	0.4	0.8
Monoiso-propanol amine	0.9	0.9
DIPA	0.25	0.6
MAE	slightly above 2	Between 4 and 4.5
EAE	slightly above 1.5	between 4 and 4.5
Morpholine	2	4
2,6-DMM	slightly above 2	between 4 and 4.5

For carbonyl sulphide substantially the same results were obtained when the experiments were repeated in a stirred reactor. Substantially the same relative rates of absorption are, moreover, obtained at any other temperature in the range from 15°C to 50°C.

As a result of these increased absorption rates a reduced amount of contacting surface is required for the absorption of a given amount of impurities as compared with the absorption of the same amount of impurities by means of conventional alkanolamines. On the other hand, in existing equipment a more complete removal of impurities can be obtained by a replacement of the conventional amines by amines according to the present invention.

The basic step in the process of the invention comprises treating the fluid with the liquid absorbent, preferably in a number of stages on the countercurrent principle.

Countercurrent contacting in an absorption column is usually preferred when treating gases and vapours. In such an operation intimate contacting is usually effected in a vertical column, the gas entering near the bottom and leaving the column near or at the top, while regenerated liquid absorbent enters near the top and "spent" liquid absorbent (containing extracted impurities) leaves at or near the bottom of the column. The column is preferably provided with fractionating trays, baffles, Raschig rings or other gas-liquid contacting means. In those cases where co-absorption of hydrocarbons will occur it may be useful to apply rectified absorption.

Other known techniques and equipment for the contacting of gaseous mixtures with liquid absorbent may also be used.

When treating liquid streams use may be made of mixers such as propeller mixers or centrifugal mixers, but other liquid-liquid extraction devices such as a packed columns or "rotating disc contactors" and the like may also be used.

The temperature at which the absorption is carried out is usually in the range

of from 15 to 70°C, and preferably from 25°C to 50°C. In multi-stage operations it may be beneficial to use a temperature gradient.

Elevated pressure may be used, if desired, e.g. to keep the fluid to be treated in the liquid phase or to keep the gas volumes to be handled sufficiently small, and/or to increase the degree of purification.

The "spent" liquid absorbent that has been used for purifying the fluid, contains physically and/or chemically dissolved impurities such as hydrogen sulphide, carbon dioxide and carbonyl sulphide, possibly together with other impurities and/or some hydrocarbons originally present in the feedstock. With respect to carbonyl sulphide it should be observed that it may partly be present in physically dissolved form and/or in the form of its chemically bound hydrolysis products hydrogen sulphide and carbon dioxide.

At least part and preferably the whole of this amine solution is re-used for the treatment of further amounts of fluids after desorptive regeneration. The term "desorptive regeneration" refers to the complete or partial desorption of hydrogen sulphide, carbon dioxide and/or carbonyl sulphide, and possibly other impurities, from the spent liquid absorbent, by means of increasing the temperature and/or lowering the pressure and/or stripping. The stripping may be carried out by direct injection of a gas or vapour (such as nitrogen or steam) or by generating vapours from the liquid absorbent. The regeneration may be effected, for example by heating the spent liquid absorbent, e.g. to a temperature of from 70°C to 130°C, at such a low pressure that the solution starts boiling as a result of which the components absorbed from the gases treated and/or the hydrolysis products formed are stripped by the vapours evolving from the boiling solution.

The regeneration of the spent absorption liquid may be carried out in conventional equipment, e.g. in a vertical regeneration or stripping column.

It may be impossible to obtain complete regeneration of the liquid absorbent by the above physical means, because there may be some formation of non-regenerable compounds, e.g. in the course of side reactions or of reactions between the amines used and impurities such as carbon disulphide and hydrocyanic acid. To prevent the building-up of such non-regenerable compounds to an unacceptably high extent it may be necessary to discard part of the spent or regenerated solvent as a bleed stream and to re-use only the remaining part of the regenerated solvent, possibly after adjustment of its composition and quantity by addition of make-up components. The bleed stream may in turn be processed by suitable physical or chemical means to recover the amines.

The following Example illustrates the invention.

EXAMPLE

A gas mixture obtained by partial combustion of hydrocarbon material by means of oxygen in the presence of steam and having the following composition (% by volume; excluding water vapour): 48.0% hydrogen; 47.4% carbon monoxide; 4.0% carbon dioxide; 0.8% hydrogen sulphide and 0.03% carbonyl sulphide was purified by means of an aqueous solution of MAE, having an amine concentration of 3.33 moles per litre.

Use was made of a vertical absorption column with a diameter of 0.36 m and provided with 25 bubble cap trays at a spacing of 0.6 m.

The gas was continuously introduced near the bottom of this column at a rate of 1000 standard cubic metres per hour (0°C, 1 atm.abs.), the inlet temperature being 40°C. Regenerated amine solution was introduced near the top of the column at a rate of 3 cubic metres per hour, its temperature also being 40°C. The absorption was carried out at 20 atm.abs.

The treated gas that left the absorption column at its top contained less than 0.1% carbon dioxide, less than 0.0005% hydrogen sulphide and less than 0.005% carbonyl sulphide.

The spent amine solution that was discharged from the bottom of the absorption column was depressurized to 1.5 atm.abs. and continuously passed to the upper part of a vertical regeneration column, which was provided with 16 bubble cap trays at a spacing of 0.6 m, the column diameter again being 0.36 m.

The bottom temperature in the regenerator was kept at about 112°C by means of indirect heating with steam. The liquid absorbent was in fact boiling at this temperature and hydrogen sulphide and carbon dioxide (and perhaps some remaining carbonyl sulphide) were stripped from the liquid absorbent by means of the steam evolving from the boiling absorbent. The desorbed impurities leave the regenerator at its top. The

regenerated liquid absorbent leaves the regenerating column at the bottom and, after cooling to 40°C, is recycled to the absorption column for the purification of further amounts of gas. The recycled solution contains less than 0.03 moles carbon dioxide and hydrogen sulphide + carbonyl sulphide per mole MAE.

WHAT WE CLAIM IS:—

1. A process for the purification of a fluid which contains hydrogen sulphide and/or carbon dioxide and/or carbonyl sulphide as impurities, which comprises treating the fluid with a liquid absorbent comprising an aqueous solution of at least one amine of the group consisting of alkanolalkyl amines and morpholines, thereby obtaining a fluid with a reduced impurity content and a liquid absorbent containing absorbed impurities, and re-using at least part of the said liquid absorbent after desorptive regeneration for treating a further quantity of the fluid to be purified.
2. A process according to claim 1 in which the amine boils between 120 and 200°C.
3. A process according to Claim 1 in which the amine boils between 135 and 180°C.
4. A process according to any of the preceding claims in which the aqueous solution comprises methylaminoethanol, and/or ethylaminoethanol and/or 2,6 dimethyl morpholine.
5. A process according to any of the preceding claims in which the amine content of the liquid absorbent is between 0.5 and 8 moles/l.
6. A process according to any of Claims 1 to 4 in which the amine content of the liquid absorbent is between 1 and 6 moles/l.
7. A process according to any of the preceding claims in which the liquid absorbent also contains a glycol.
8. A process according to any of the preceding claims in which the fluid to be purified is treated with the liquid absorbent countercurrently in a number of stages.
9. A process according to any of the preceding claims in which the fluid to be purified is treated with the liquid absorbent at a temperature in the range 15 to 70°C.
10. A process according to any of Claims 1 to 8 in which the fluid to be purified is treated with the liquid absorbent at a temperature in the range 25 to 50°C.
11. A process according to any of the preceding claims in which the fluid to be purified is treated with the liquid absorbent in multi-stage operation using a temperature gradient.
12. A process according to any of the preceding claims in which the fluid to be purified is treated with the liquid absorbent at elevated pressure.
13. A process as claimed in any of the preceding claims in which the desorptive regeneration is effected by heating the spent liquid absorbent to a temperature of from 70°C to 130°C at such a low pressure that the solution starts boiling.
14. A modification of the process as claimed in any of the preceding claims in which the fluid to be purified is treated with a liquid absorbent comprising at least one amine of the group consisting of alkanolalkyl amines and morpholines and at least one physical solvent for the impurities to be removed from the feed material, thereby obtaining a fluid with a reduced impurity content and a liquid absorbent containing absorbed impurities, and re-using at least part of the said liquid absorbent after desorptive regeneration for treating a further quantity of the fluid to be purified.
15. A process according to Claim 14 in which the liquid absorbent also contains water.
16. A process according to Claim 15 in which the water content of the liquid absorbent is in the range 1 to 30 wt.-%.
17. A process according to any of Claims 14, 15 and 16 in which the physical solvent is (or the physical solvents are) thiophene tetrahydro-1, 1-dioxide and/or dimethyl formamide and/or N-methyl pyrrolidone.
18. A process for the removal of acidic and/or sulphur-containing gases from a gaseous mixture which comprises treating the gaseous mixture with a liquid absorbent comprising an aqueous solution of methylaminoethanol.
19. A process according to Claim 18 in which the gaseous mixture comprises carbonyl sulphide
20. A process for the purification of a fluid substantially as described in the Example.
21. Fluids which have been purified by a process as claimed in any of the preceding claims.
22. Acidic and sulphur-containing gases which have been removed as impurities from other fluids, by a process as claimed in any of Claims 1 to 20.

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